Electronic Supplementary Information

Core Expanded, 21,23-Dithiadiacenaphtho[1,2-c]porphyrin Interactions with [60]fullerene

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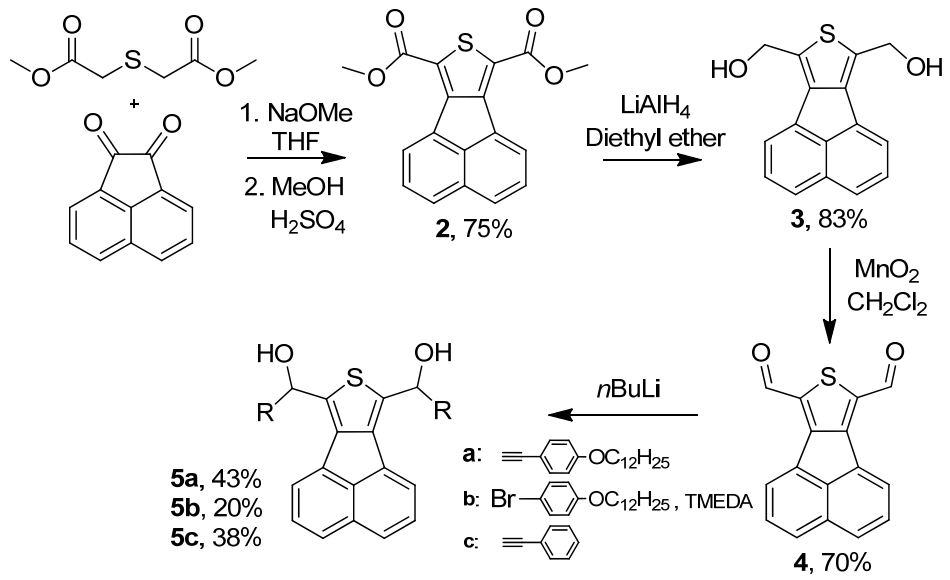


Scheme 1: Synthesis of 21,23-Dithiadiacenaphtho[1,2-*c*]porphyrin precursors **5a**, **5b** and **5c**.

Dimethyl 2,2'-thiodiacetate: Methylchloroacetate (2.3 mL, 29.5 mmol) was dissolved in methanol (50 mL) and brought to reflux. From a dropping funnel, a solution of sodium sulfide nonahydrate (3.5 g, 14.7 mmol) in water (20 mL) was added over 30 minutes to the hot methanol solution. After complete addition, the entire solution was refluxed an additional 1 h. After cooling to room temperature, the methanol was removed under reduced pressure and the aqueous solution was extracted with ethyl acetate (3 × 50 mL). The organic portions were then combined, washed with saturated sodium bicarbonate solution (3 × 20 mL) followed by drying over anhydrous Na_2SO_4. Removal of ethyl acetate under reduced pressure afforded dimethyl 2,2'-thiodiacetate as a colourless oil (1.8 g, 70%), which was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 6H), 3.33 (s, 4H).

Acenaphtho[1,2-*c*]thiophene-7,9-dimethyl ester (**2**): Dimethyl 2,2'-thiodiacetate (5.9 g, 33 mmol) and acenaphthenequinone (6.7 g, 37 mmol) were combined in freshly dried THF (100 mL). To this solution, sodium methoxide (4.5 g, 83 mmol) was added and the solution turned dark purple. The mixture was stirred under a nitrogen atmosphere at room temperature for 5 days at which point the THF was removed under reduced pressure. An excess of MeOH (100 mL) and H_2SO_4 (5 mL) was added to the brown solid and the solution was allowed to reflux for an additional 24 h. The solution was cooled and the MeOH was removed under reduced pressure. The brown solid was suspended in water and suction filtered followed by recrystallization from refluxing THF. Acenaphtho[1,2-*c*]thiophene-7,9-dimethyl ester was obtained as a brown powder (8.0 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.1 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 2H), 4.03 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 98.7, 95.3, 93.0, 90.7, 90.6, 90.0, 89.9, 89.4, 89.3, 71.0. HR-MS (MALDI-TOF): calcd for $C_{18}H_{12}O_4S^+$ $[M]^+$ 324.0451, found 324.0444.

Acenaphtho[1,2-*c*]thiophene-7,9-dimethanol (**3**): Acenaphtho[1,2-*c*]thiophene-7,9-dimethyl ester (125 mg, 0.4 mmol) was dissolved in diethyl ether (50 mL) in a flame dried Schlenk flask

and cooled to -78 °C under a nitrogen atmosphere. To this solution, lithium aluminum hydride (37 mg, 1.0 mmol) was added and the mixture was allowed to warm to room temperature and stir overnight (~18 h). The mixture was quenched at 0 °C with 1 M HCl and filtered to collect a light brown solid. Recrystallization from refluxing $CHCl_3$ afforded acenaphtho[1,2-*c*]thiophene-7,9-dimethanol as a light tan powder (87 mg, 83%). ^{1}H NMR (400 MHz, DMSO) δ 7.77 (t, *J* = 6.9 Hz, 4H), 7.58 (dd, *J* = 8.1, 7.1 Hz, 2H), 5.71 (s, 2H), 4.90 (s, 4H).

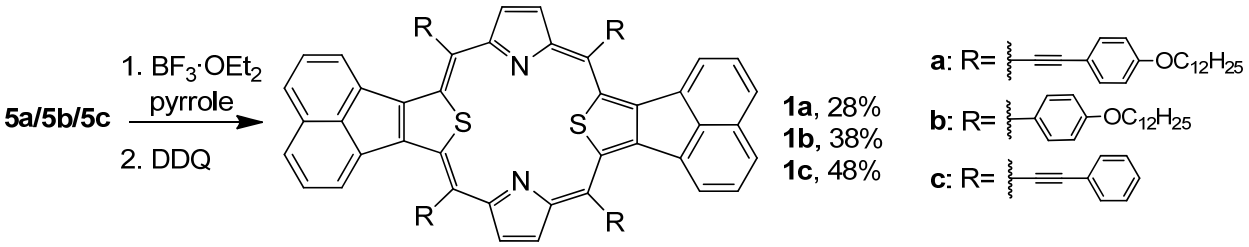
Acenaphtho[1,2-*c*]thiophene-7,9-dicarboxaldehyde (**4**): Acenaphtho[1,2-*c*]thiophene-7,9-dimethanol (100 mg, 0.4 mmol) and MnO_2 (0.5 g, 5.6 mmol) were suspended in $CHCl_3$ (50 mL) and stirred for 5 h at room temperature. The solution was then extracted with $CHCl_3$ (3 × 50 mL) and washed with water (3 × 50 mL). The organic extracts were dried with anhydrous Na_2SO_4 and the $CHCl_3$ was removed under reduced pressure to afford a yellow powder. Recrystallization from refluxing $CHCl_3$ afforded acenaphtho[1,2-*c*]thiophene-7,9-dicarboxaldehyde as a fluffy yellow solid (69 mg, 70%). ^{1}H NMR (402 MHz, $CDCl_3$) δ 10.32 (s, 2H), 8.43 (d, *J* = 7.1 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.72 (dd, *J* = 8.1, 7.3 Hz, 2H).

Acenaphtho[1,2-*c*]thiophene-7,9-bis[(4-dodecyloxyethynylphenyl)hydroxymethyl] (**5a**): 4-Dodecyloxyethynylbenzene (0.4 g, 1.5 mmol) was added to diethyl ether (20 mL) and cooled to -78 °C. Under a nitrogen atmosphere, TMEDA (0.2 mL, 1.5 mmol) and *n*-BuLi (0.6 mL of a 2.5 M solution in hexanes, 1.5 mmol) were added to the initial solution and stirred for 1 h. In a separate flask, acenaphtho[1,2-*c*]thiophene-7,9-dicarboxaldehyde (182 mg, 0.7 mmol) was added to diethyl ether (20 mL) and cooled to 0 °C in an ice bath, under nitrogen, 5 mins before the initial hour concluded. The cooled mixture of lithiated 4-dodecyloxyethynylbenzene in diethyl ether was then transferred via cannula to the cooled solution of acenaphtho[1,2-*c*]thiophene-7,9-dicarboxaldehyde. The resulting solution was allowed to warm to room temperature over 1 h upon which it was quenched with water and extracted with diethyl ether (3 × 20 mL). The organic extracts were combined and dried over anhydrous Na_2SO_4 after which the diethyl ether was removed under reduced pressure. The resulting crude oil was purified by column chromatography using hexanes and ethyl acetate gradient (4:1 to 2:1) to afford acenaphtho[1,2-*c*]thiophene-7,9-bis[(4-dodecyloxyethynylphenyl)hydroxymethyl] as a pure yellow oil (250 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.57 (dd, *J* = 8.1, 7.2 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 4H), 6.81 (d, *J* = 8.8 Hz, 4H), 6.20 (s, 2H), 3.94 (t, *J* = 6.6 Hz, 4H), 2.59 (s, 2H), 1.82 – 1.71 (m, 4H), 1.50 – 1.38 (m, 4H), 1.36 – 1.20 (m, 32H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 141.7, 139.7, 133.8, 133.5, 132.4, 131.0, 127.8, 125.7, 121.6, 114.6, 113.9, 86.6, 86.3, 68.2, 60.0, 32.1, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.3, 26.1, 22.8, 14.3. HR-MS (ESI): calcd for $C_{56}H_{68}O_4SNa^+$ $[M+Na]^+$ 859.4731, found 859.4744.

Acenaphtho[1,2-*c*]thiophene-7,9-bis[(4-dodecyloxyphenyl)hydroxymethyl] (**5b**): 1-Bromo-4-dodecyloxybenzene (258 mg, 0.8 mmol) was added to freshly dried THF (20 mL) and cooled to -78 °C. Under a nitrogen atmosphere, *n*-BuLi (0.3 mL of a 2.5 M solution in hexanes, 0.8 mmol) were added to the initial solution and stirred for 1 h. In a separate flask, acenaphtho[1,2-*c*]thiophene-7,9-dicarboxaldehyde (91 mg, 0.3 mmol) was added to THF (20 mL) and cooled to 0 °C in an ice bath, under nitrogen, 5 mins before the initial hour concluded. The cooled mixture

of lithiated 1-bromo-4-dodecyloxybenzene in diethyl ether was then transferred via cannula to the cooled solution of acenaphtho[1,2-*c*]thiophene-7,9-dicarboxaldehyde. The resulting solution was allowed to warm to room temperature over 1 h upon which it was quenched with water and extracted with diethyl ether (3 × 20 mL). The organic extracts were combined and dried over anhydrous Na_2SO_4 after which the diethyl ether was removed under reduced pressure. The resulting crude oil was subjected to column chromatography using hexanes and ethyl acetate gradient (4:1 to 2:1) to afford acenaphtho[1,2-*c*]thiophene-7,9-bis[(4-dodecyloxyphenyl)hydroxymethyl] as a yellow oil (120 mg, 20%), which was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 2H), 8.22 (s, 1H), 8.20 (s, 1H), 7.91 (s, 1H), 7.89 (s, 1H), 7.61 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.47 – 7.39 (m, 4H), 6.87 – 6.77 (m, 4H), 6.26 (s, 1H), 6.22 (s, 1H), 3.88 (t, *J* = 6.6 Hz, 4H), 2.83 (d, *J* = 8.3 Hz, 2H), 1.78 – 1.68 (m, 4H), 1.46 – 1.18 (m, 36H), 0.92 – 0.85 (m, 6H). HR-MS (ESI): calcd for $C_{52}H_{67}O_3S^+$ $[M\text{-}OH]^+$ 771.4805, found 771.4767.

Acenaphtho[1,2-*c*]thiophene-7,9-bis[(4-ethynylphenyl)hydroxymethyl] (**5c**): Phenyl acetylene (0.1 mL, 0.8 mmol) was added to diethyl ether (20 mL) and cooled to -78 °C. Under a nitrogen atmosphere, TMEDA (0.2 mL, 0.8 mmol) and *n*BuLi (0.4 mL of a 2.5 M solution in hexanes, 0.8 mmol) were added to the initial solution and stirred for 1 h. In a separate flask, acenaphtho[1,2-*c*]thiophene-7,9-dicarboxaldehyde (118 mg, 0.4 mmol) was added to diethyl ether (20 mL) and cooled to 0 °C in an ice bath, under nitrogen, 5 mins before the initial hour concluded. The cooled mixture of lithiated phenyl acetylene in diethyl ether was then transferred via cannula to the cooled solution of acenaphtho[1,2-*c*]thiophene-7,9-dicarboxaldehyde. The resulting solution was allowed to warm to room temperature over 1 h upon which it was quenched with water and extracted with diethyl ether (3 × 20 mL). The organic extracts were combined and dried over Na_2SO_4 after which the diethyl ether was removed under reduced pressure. The resulting crude oil was subjected to column chromatography using hexanes and ethyl acetate gradient (4:1 to 2:1) to afford acenaphtho[1,2-*c*]thiophene-7,9-bis[(4-ethynylphenyl)hydroxymethyl] as a yellow powder (67 mg, 38%). ^{1}H NMR (402 MHz, MeOD) δ 8.02 (d, *J* = 7.0, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.62 (dd, *J*=8.1, 7.2 2H), 7.51 – 7.48 (m, 4H), 7.38 – 7.34 (m, 6H), 6.27 (d, *J* = 4.4 Hz, 2H). ^{13}C NMR (101 MHz, MeOD) δ 142.2, 140.9, 135.8, 133.8, 132.7, 132.6, 129.8, 129.5, 128.8, 126.6, 123.8, 122.6, 89.4, 86.2, 60.1. HR-MS (ESI): calcd for $C_{32}H_{20}O_2SNa$ $[M+Na]^+$ 491.1070, found 491.1076.

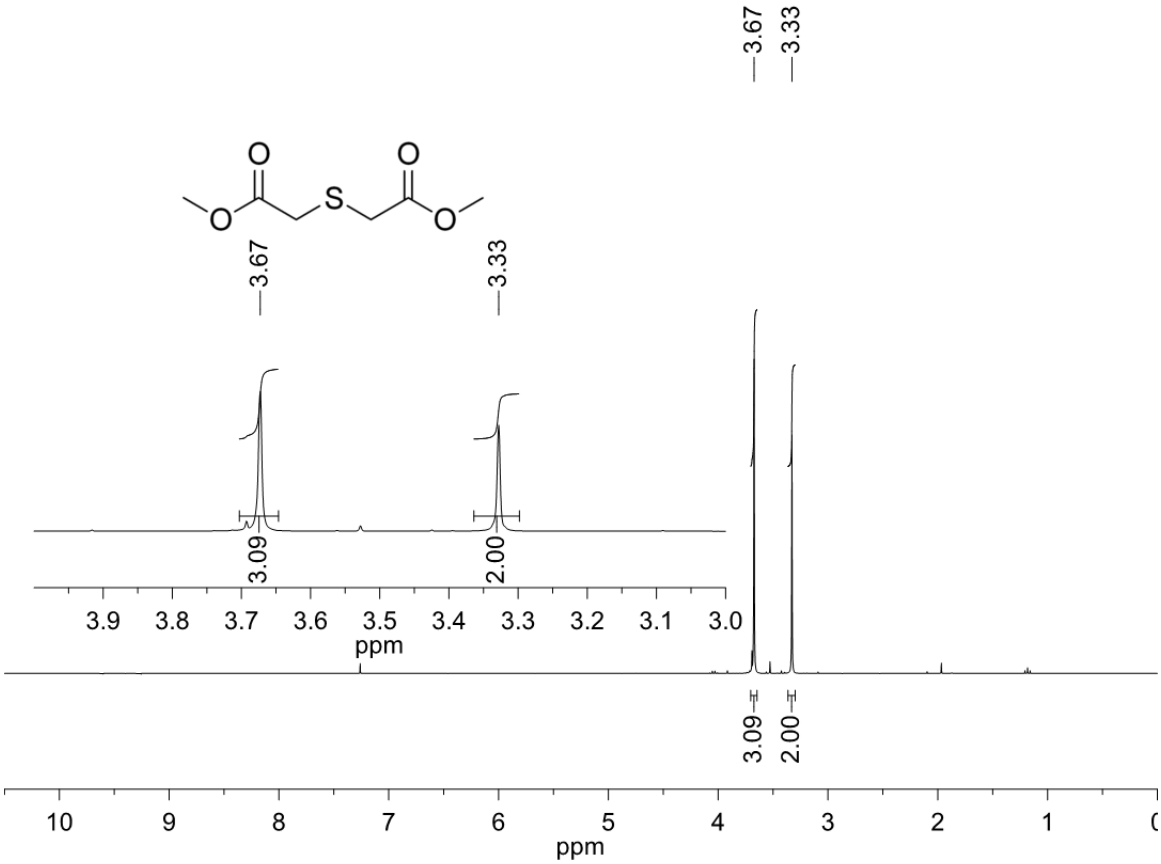


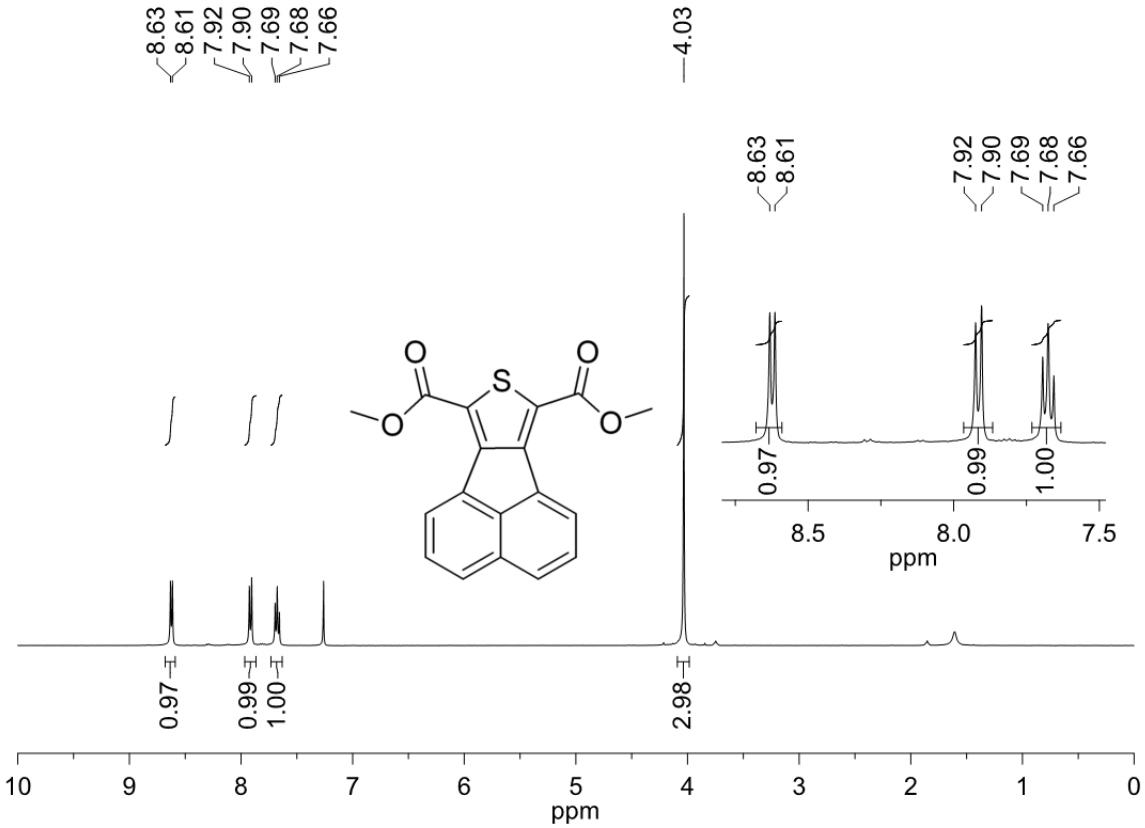
Scheme 2: Synthesis of 21,23-dithiadiacenaphtho[1,2-c]porphyrins **1a**, **1b** and **1c**.

5,10,15,20-Tetra(4-dodecyloxyethynylphenyl)-21,23-dithiadiacenaphtho[1,2-*c*]porphyrin (**1a**): The dialcohol acenaphtho[1,2-*c*]thiophene-7,9-bis[(4-dodecyloxyethynylphenyl)hydroxymethyl] (207 mg, 0.25 mmol) and freshly distilled pyrrole (17 µL, 0.25 mmol) were added under nitrogen to methylene chloride (100 mL to achieve a concentration of 2.5 mM). The flask was wrapped in tin foil, then $BF_3{\cdot}OEt_2$ (13 µL, 0.1 mmol) was added and let stir no longer than 5 min. DDQ (168 mg, 0.74 mmol) was then added and let stir in ambient atmosphere for no longer than 5 min. The resulting mixture was then filtered through an alumina filter plug using methylene chloride as eluent. The methylene chloride was removed under reduced pressure and the resulting crude pink/black waxy solid was subjected to column chromatography using methylene chloride and methanol (4.5:0.5) to afford 5,10,15,20-tetra(4-dodecyloxyethynylphenyl)-21,23-dithiadiacenaphtho[1,2-*c*]porphyrin as a pink powder (61 mg, 14%, decomp. >180 °C). HR-MS (MALDI-TOF): calcd for $C_{120}H_{132}O_4N_2S_2$ $[M+H]^+$ 1729.9701, found 1729.9632.

5,10,15,20-Tetra(4-dodecyloxyphenyl)-21,23-dithiadiacenaphtho[1,2-*c*]porphyrin (**1b**): The dialcohol acenaphtho[1,2-*c*]thiophene-7,9-bis[(4-dodecyloxyphenyl)hydroxymethyl] (76 mg, 0.1 mmol) and freshly distilled pyrrole (7 µL, 0.1 mmol) were added under nitrogen to methylene chloride (40 mL to achieve a concentration of 2.5 mM). The flask was wrapped in tin foil, then $BF_3{\cdot}OEt_2$ (5 µL, 0.04 mmol) was added and let stir no longer than 5 min. DDQ (65 mg, 0.3 mmol) was then added and let stir in ambient atmosphere for no longer than 5 min. The resulting mixture was then filtered through an alumina slug using methylene chloride as eluent. The methylene chloride was removed under reduced pressure and the resulting crude pink/black waxy solid was subjected to column chromatography using methylene chloride and methanol (4.5:0.5) to afford 5,10,15,20-tetra(4-dodecyloxyphenyl)-21,23-dithiadiacenaphtho[1,2-*c*]porphyrin as a pink powder (31 mg, 19%, mp. 155-165 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.5 Hz, 8H), 8.28 (s, 4H), 7.67 (d, *J* = 8.0 Hz, 4H), 7.34 (d, *J* = 8.6 Hz, 8H), 7.21 (t, *J* = 7.7 Hz, 4H), 6.20 (d, *J* = 7.3 Hz, 4H), 4.23 (t, *J* = 6.5 Hz, 8H), 2.03 – 1.92 (m, 8H), 1.66 – 1.55 (m, 8H), 1.46 – 1.29 (m, 64H), 0.96 – 0.85 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 159.1, 148.6, 138.7, 137.3, 136.5, 135.4, 134.1, 133.9, 132.4, 129.7, 127.6, 127.4, 126.1, 115.0, 68.5, 31.9, 29.7, 29.7, 29.7, 29.7, 29.5, 29.4, 29.3, 26.2, 22.7, 14.1. HR-MS (MALDI-TOF): calcd for $C_{112}H_{132}O_4N_2S_2$ $[M+H]^+$ 1633.9701, found 1633.9637.

5,10,15,20-Tetra(4-ethynylphenyl)-21,23-dithiadiacenaphtho[1,2-*c*]porphyrin (**1c**): The dialcohol acenaphtho[1,2-*c*]thiophene-7,9-bis[(4-ethynylphenyl)hydroxymethyl] (56 mg, 0.12 mmol) and freshly distilled pyrrole (8 µL, 0.12 mmol) were added under nitrogen to methylene chloride (50 mL to achieve a concentration of 2.5 mM). The flask was wrapped in tin foil, then $BF_3{\cdot}OEt_2$ (6 µL, 0.05 mmol) was added and let stir no longer than 5 min. DDQ (81 mg, 0.4 mmol) was then added and let stir in ambient atmosphere for no longer than 5 min. The resulting mixture was then filtered through an alumina slug using methylene chloride as eluent. The methylene chloride was removed under reduced pressure and the resulting crude pink/black powder was subjected to column chromatography using methylene chloride and methanol (4.5:0.5) to afford 5,10,15,20-tetra(4-ethynylphenyl)-21,23-dithiadiacenaphtho[1,2-c]porphyrin as a pink powder (29 mg, 24%). HR-MS (MALDI-TOF): calcd for $C_{72}H_{36}N_2S_2$ $[M+H]^+$ 993.2393, found 993.2416.

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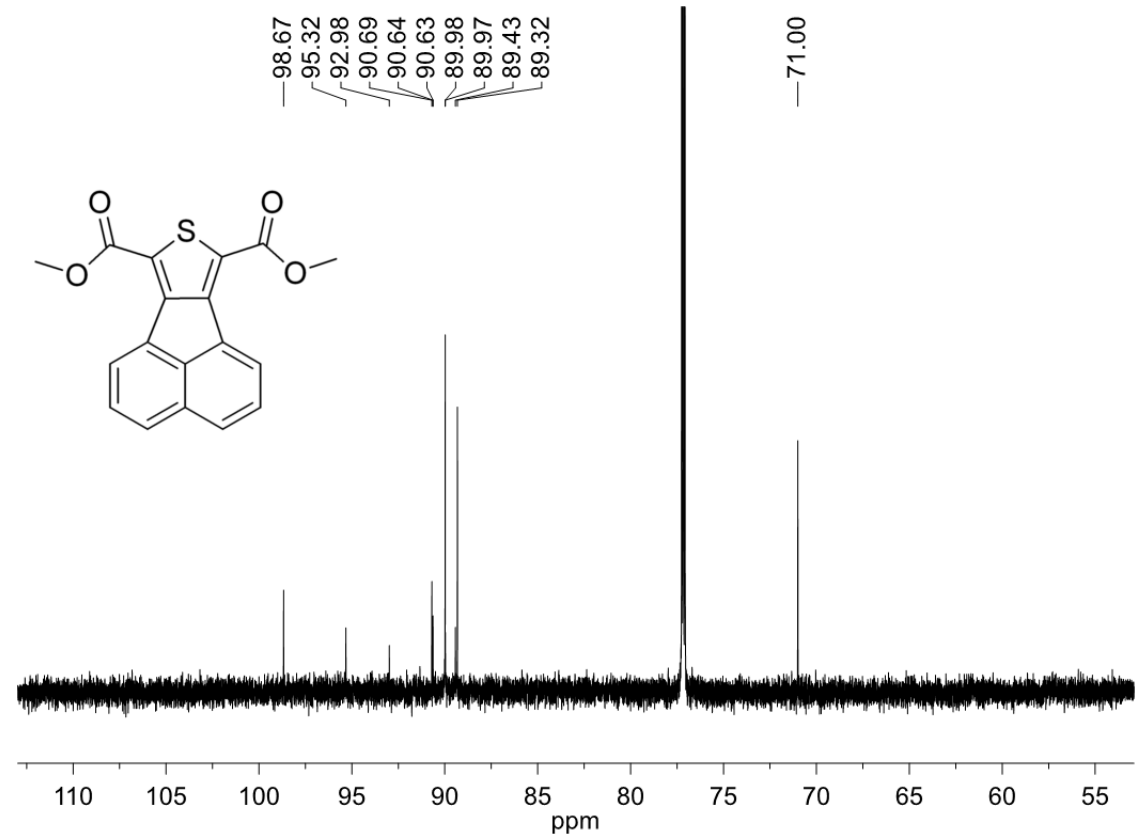
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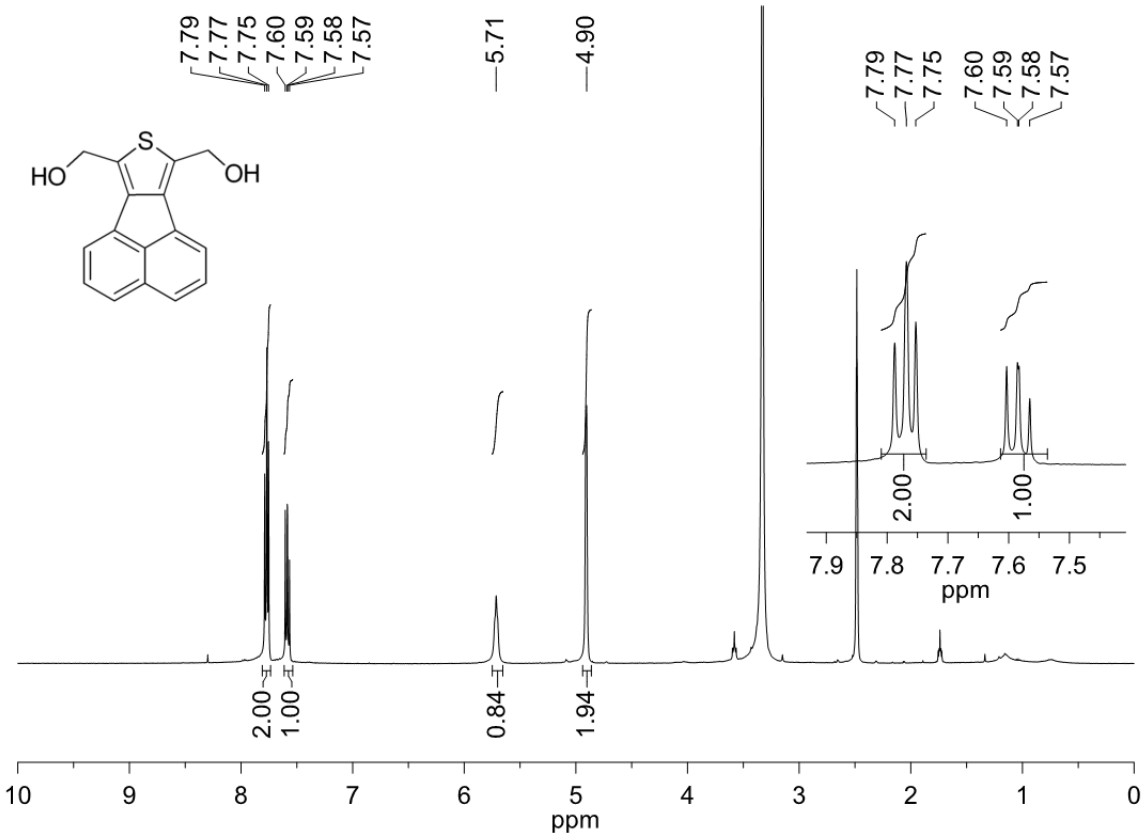
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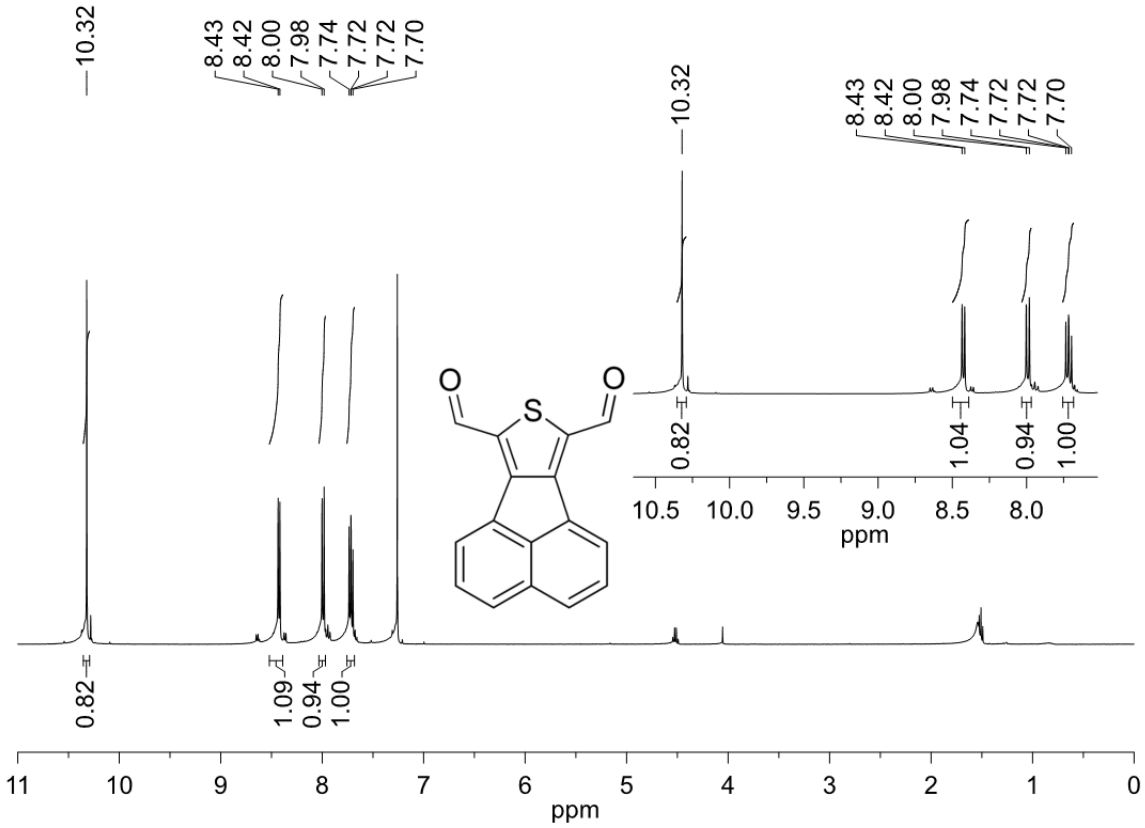
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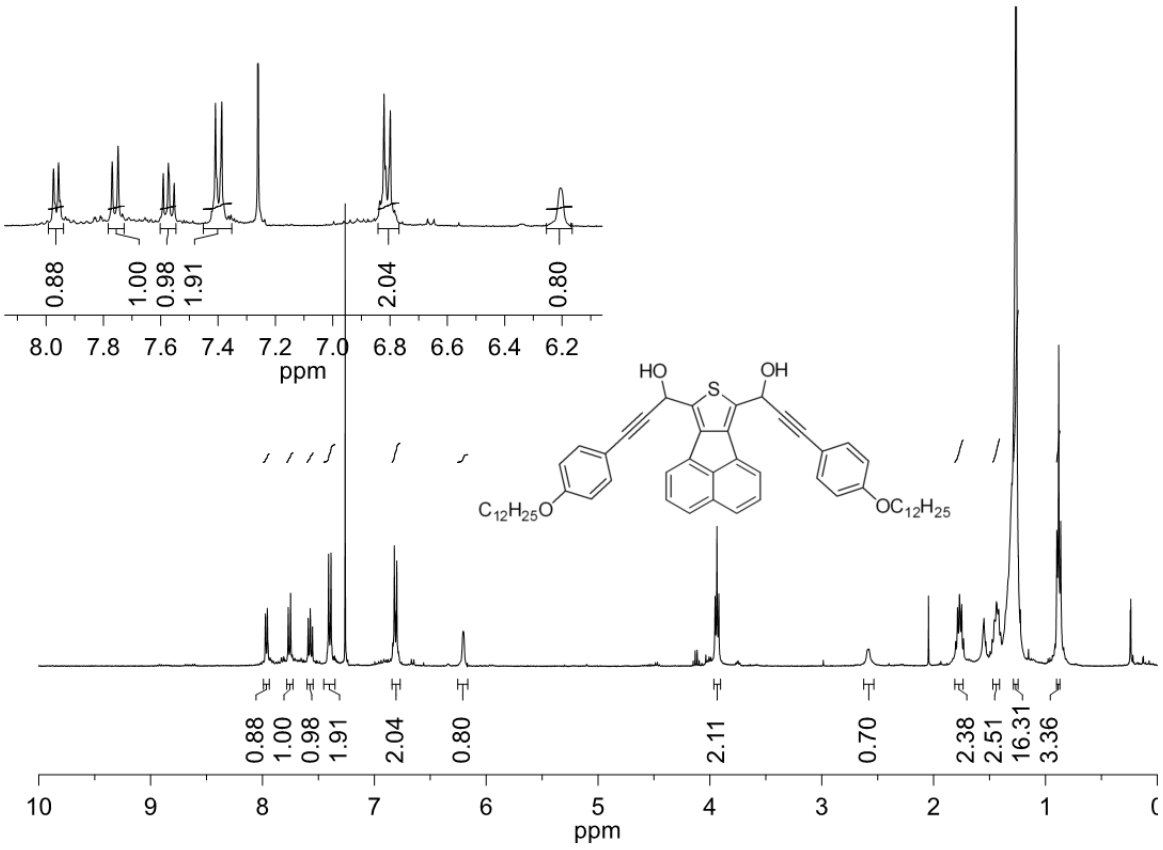
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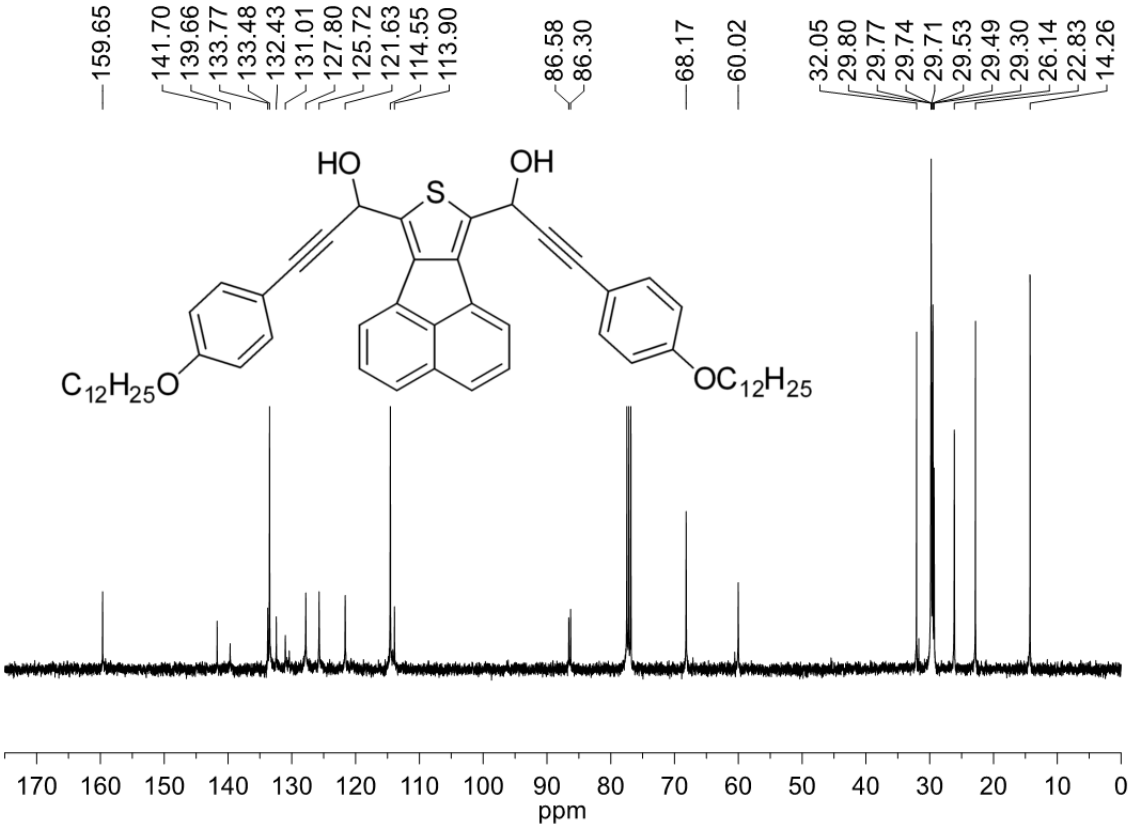
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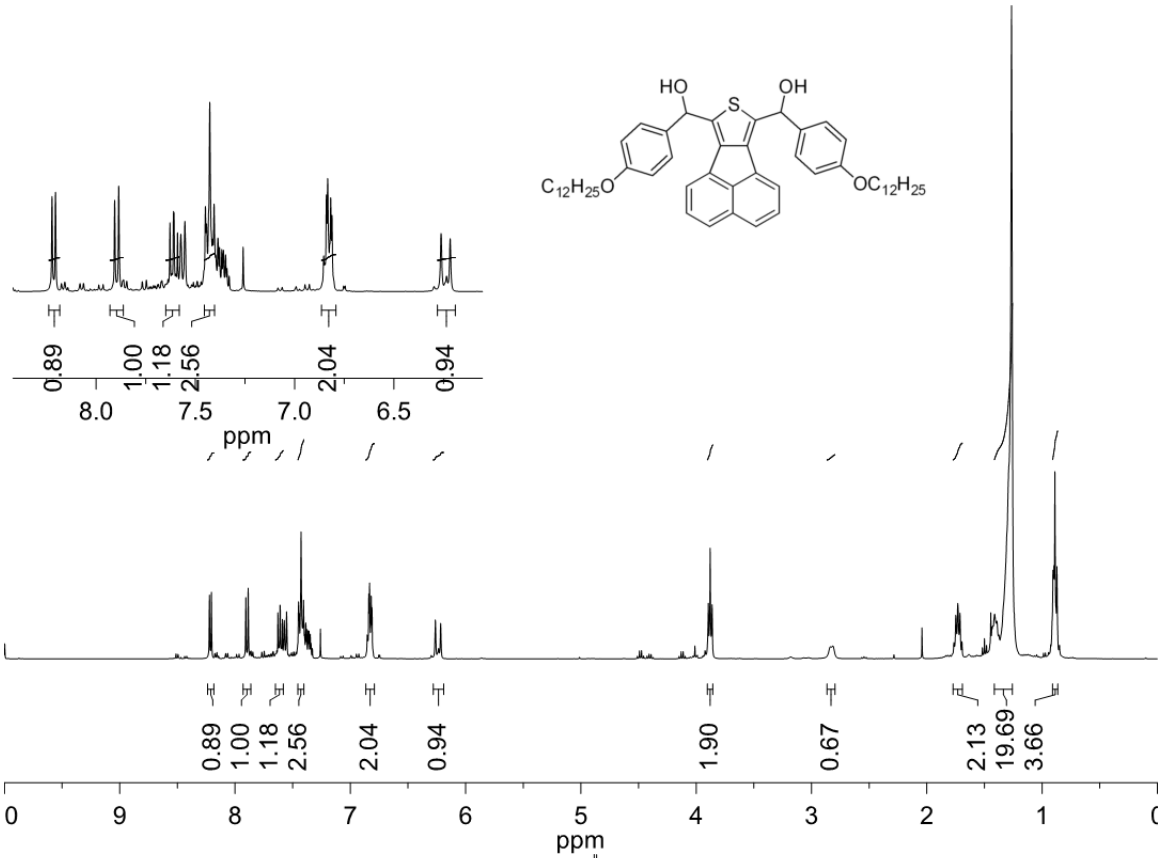
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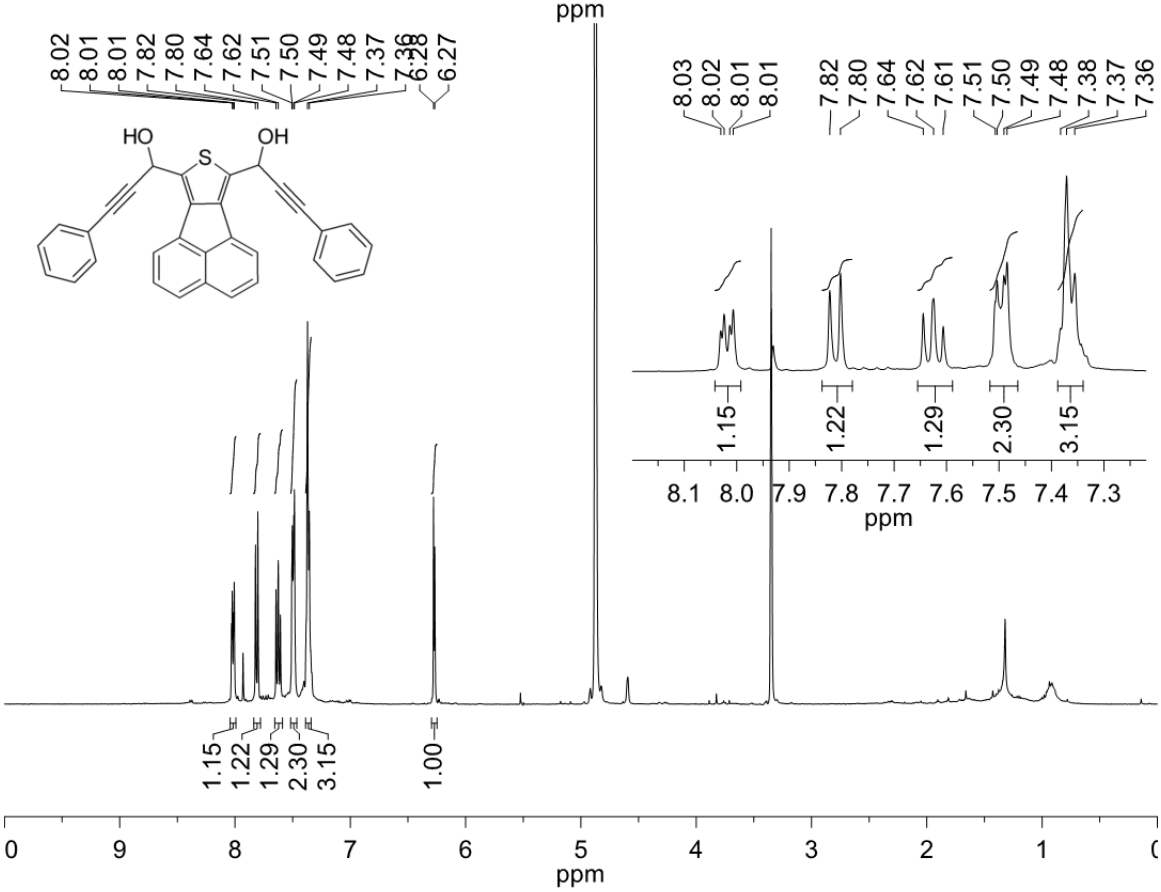
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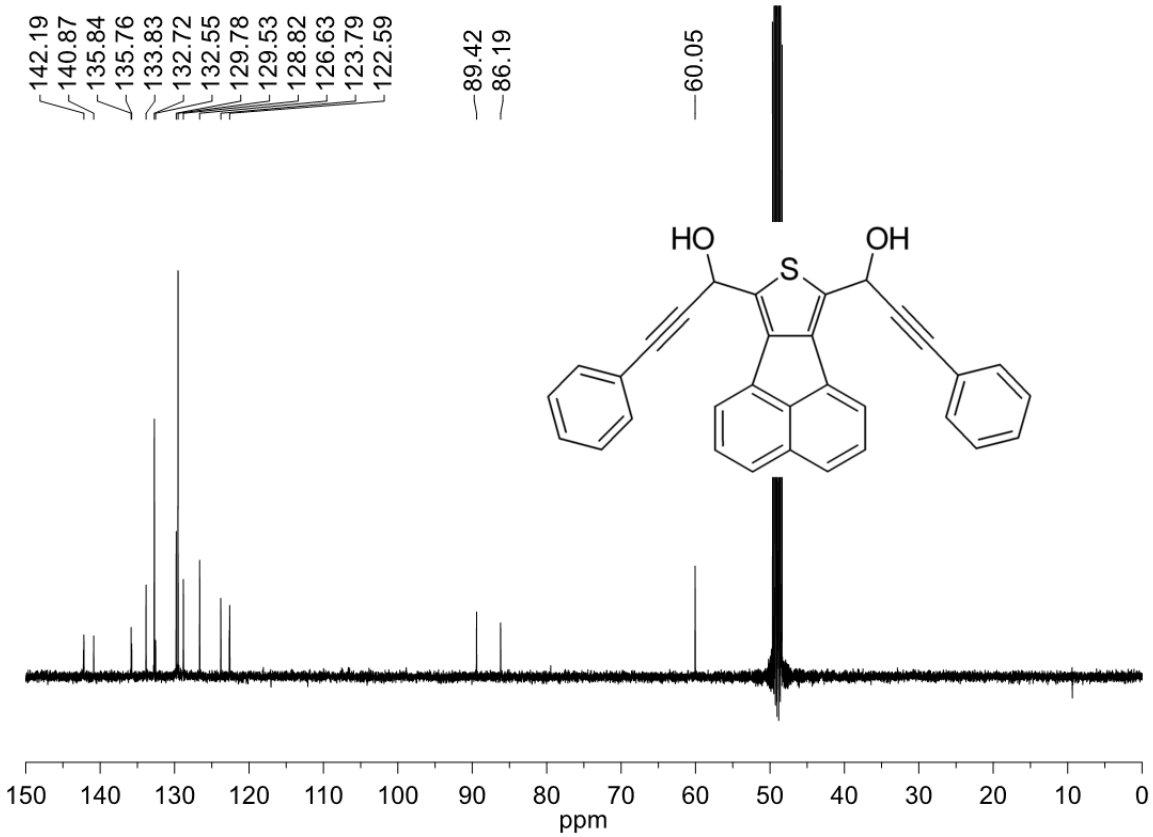
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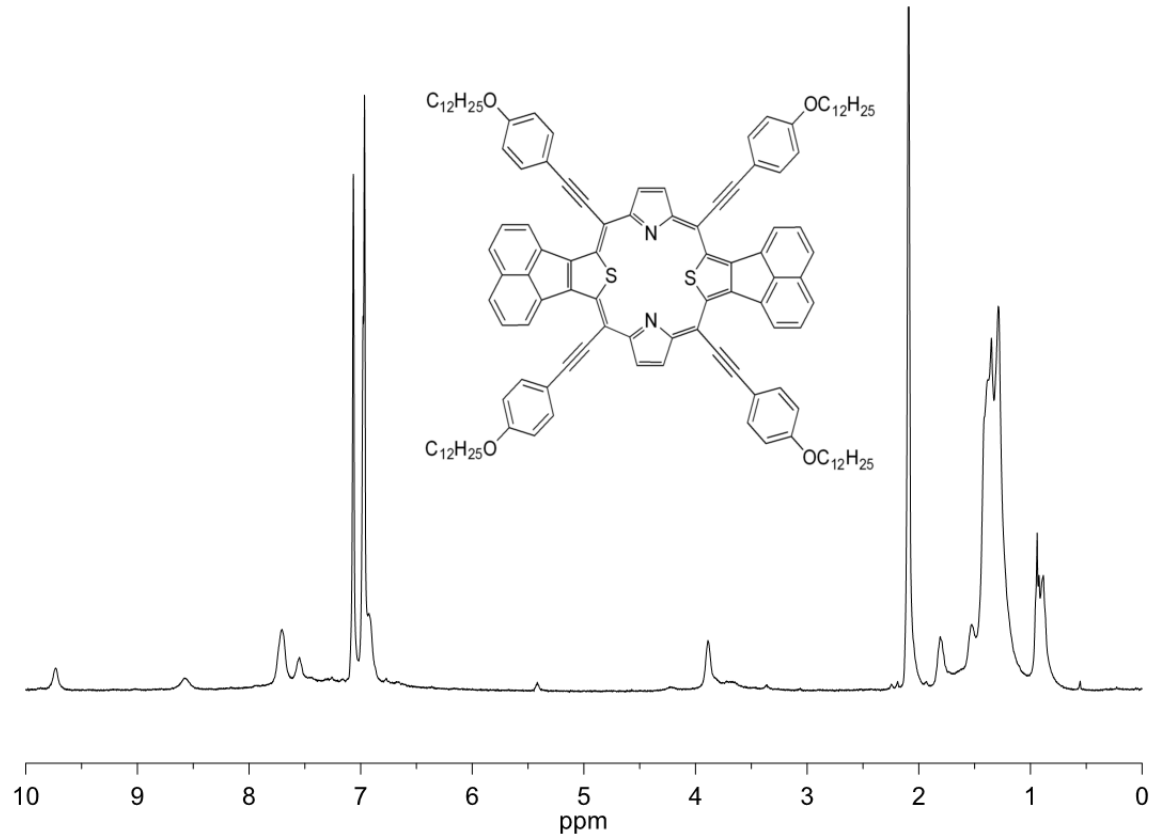
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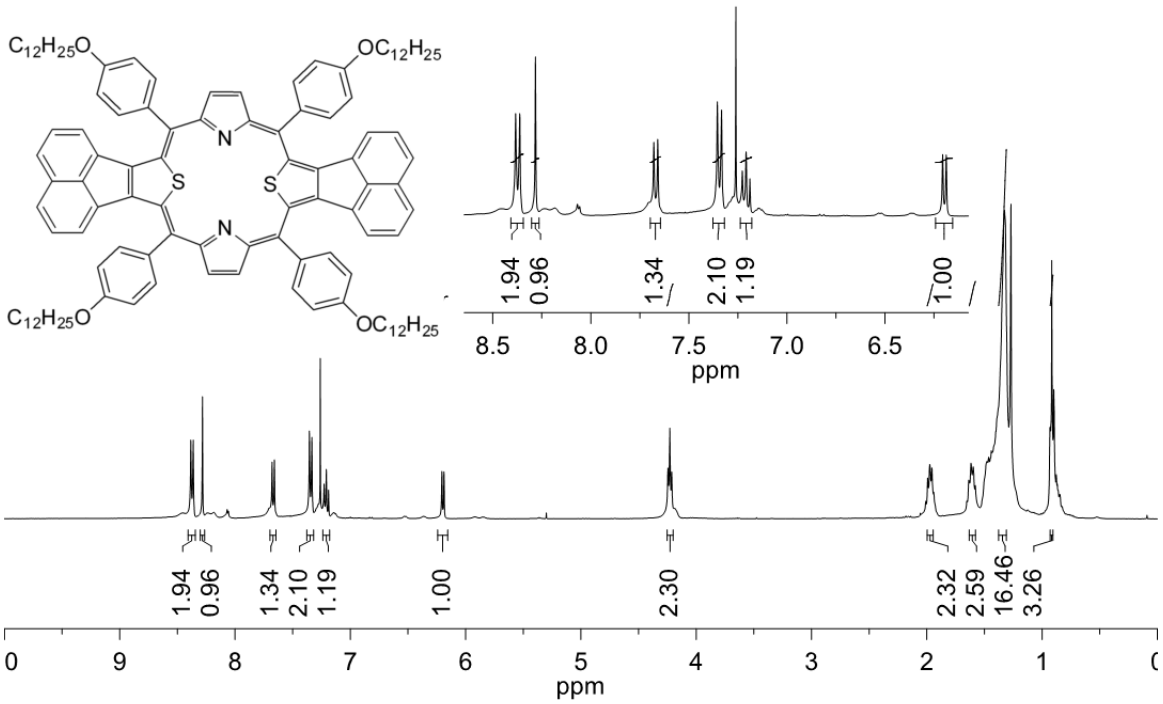
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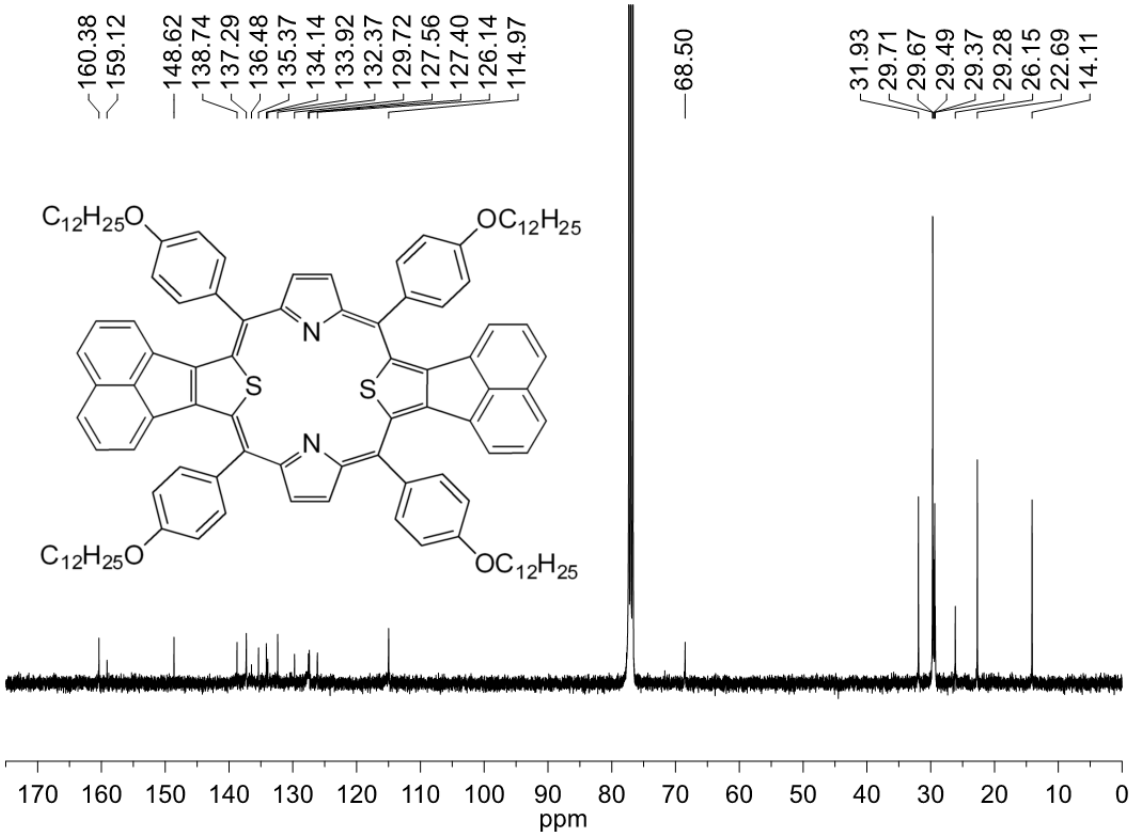
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$OC_{12}H_{25}$
N
S
S
N
$C_{12}H_{25}O$
$OC_{12}H_{25}$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

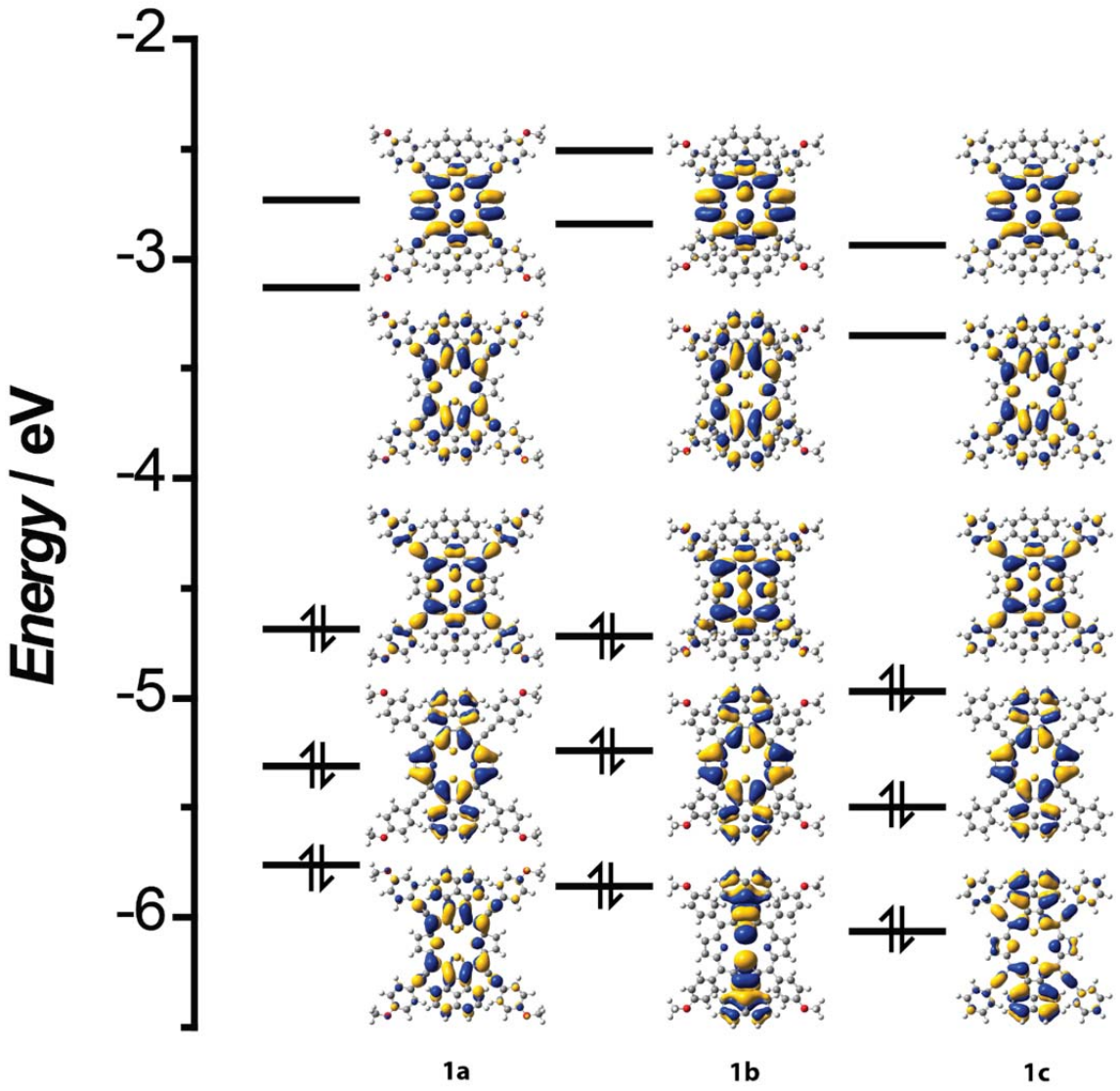

Figure S1: DFT Calculations of porphyrins **1a-c** at the B3LYP 6-31G+(d) and frontier molecular orbitals HOMO-2, HOMO-1, HOMO, LUMO and LUMO+1.

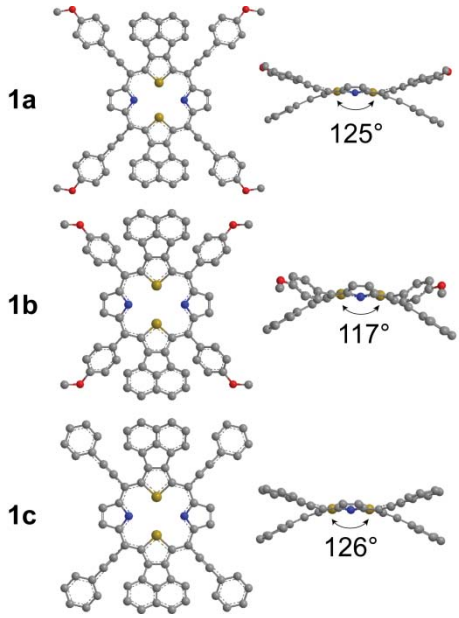

Figure S2: Optimized geometries of porphyrins **1a-c** using DFT at the B3LYP 6-31G+(d) level. First column depicts the "boat" conformation from a top view and the second column shows the same structure from the side view and the angle formed between intersecting planes of the acenaphthyl groups using CCDC Mercury 3.1 software.

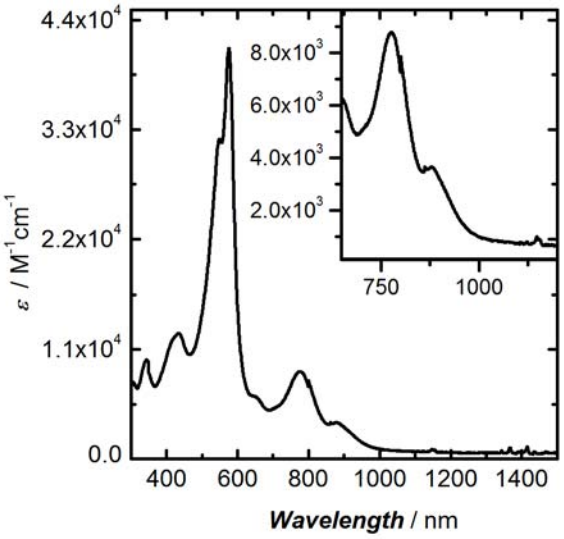

Figure S3: Porphyrin **1a** UV-Vis absorption profile in methylene chloride.

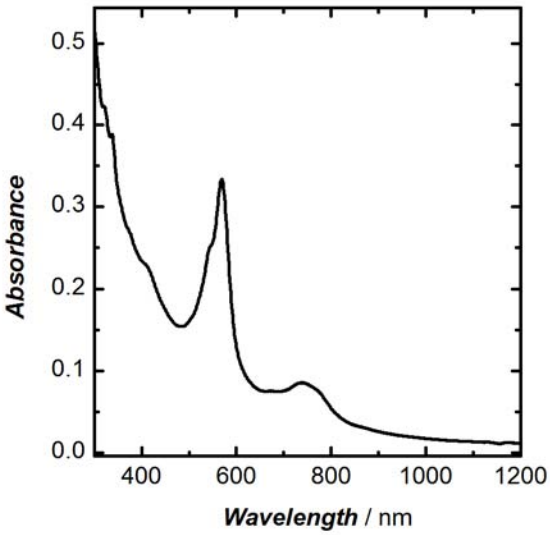

Figure S4: Porphyrin **1c** UV-Vis absorption profile in methylene chloride.

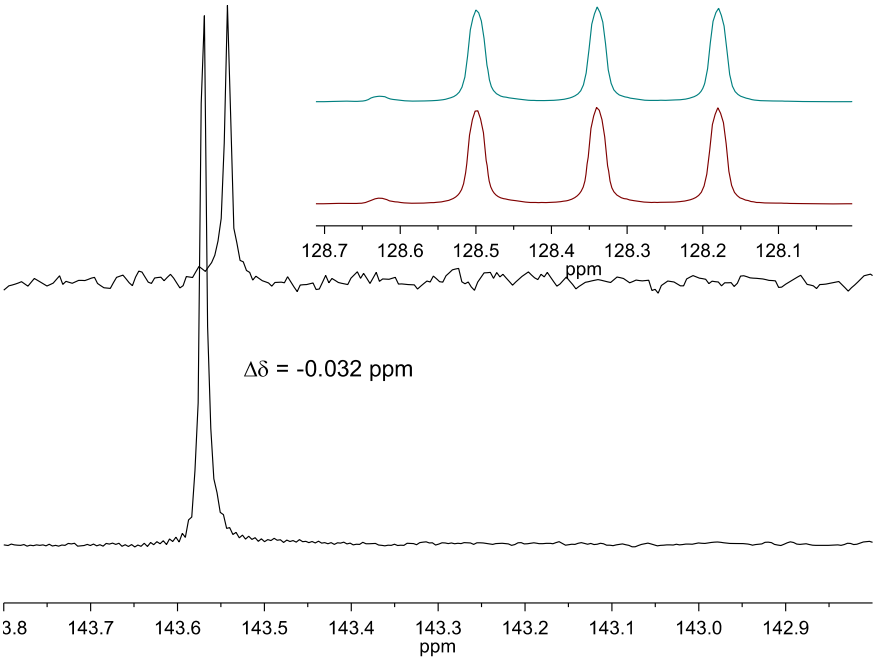

Figure S5: ^{13}C NMR (151 MHz) in toluene-d_8 of bottom) C_{60} and top) C_{60} and porphyrin **1b** in 1:1 ratio at a total concentration of 2 x 10^{-4} M. Inset shows the overlapping of toluene-d_8 solvent signals.

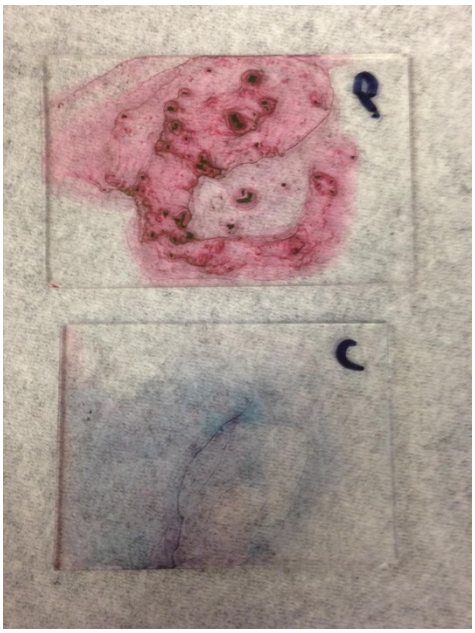

Figure S6: Solid state thin films of top) porphyrin **1b** and bottom) **1b** mixed with C_{60} at a 1:1 ratio.

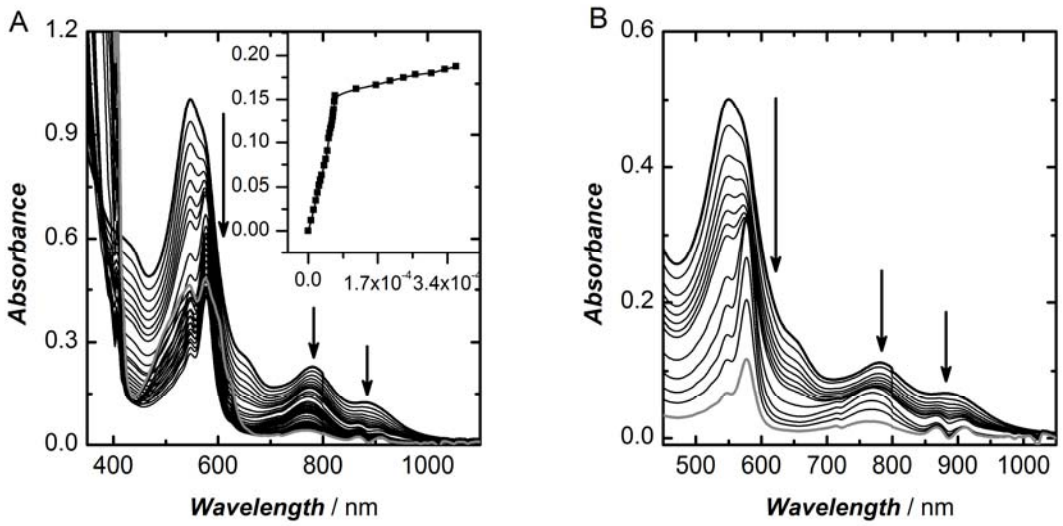

Figure S7: C_{60} (8.0×10^{-5} M) titration into A: **1a** (1×10^{-5} M) in methylene chloride. Inset: Change in absorbance at 780 nm versus concentration of C_{60} added. B: **1a** (6×10^{-6} M) in methylene chloride, titrated with neat toluene to illustrate a dilution control to show similarities in the spectrum with that of the titration of C_{60}, indicating aggregation-induced optical effects.

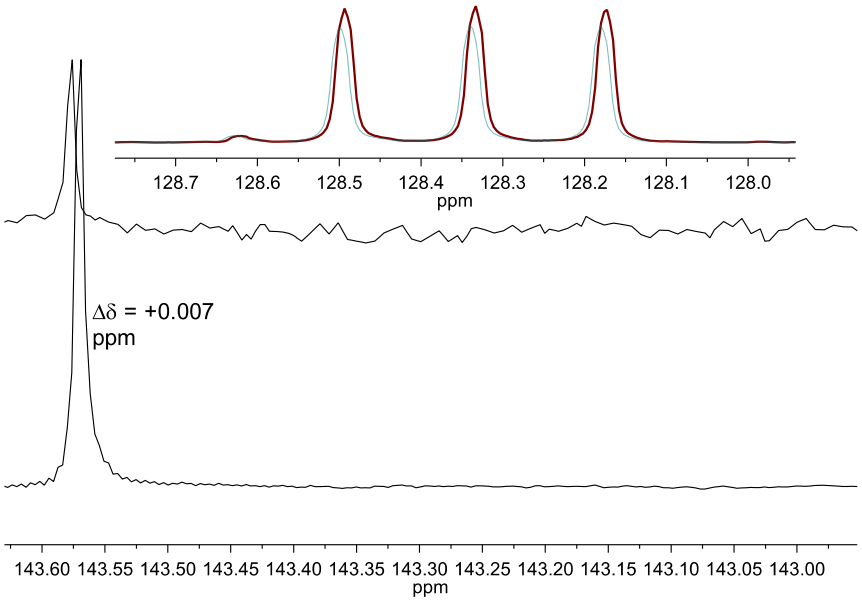

Figure S8: ^{13}C NMR (151 MHz) in toluene-d_8 of bottom) C_{60} and top) C_{60} and porphyrin **1a** in 1:1 ratio at a total concentration of 2 x 10^{-4} M. Inset shows the overlapping of toluene-d_8 solvent signals.

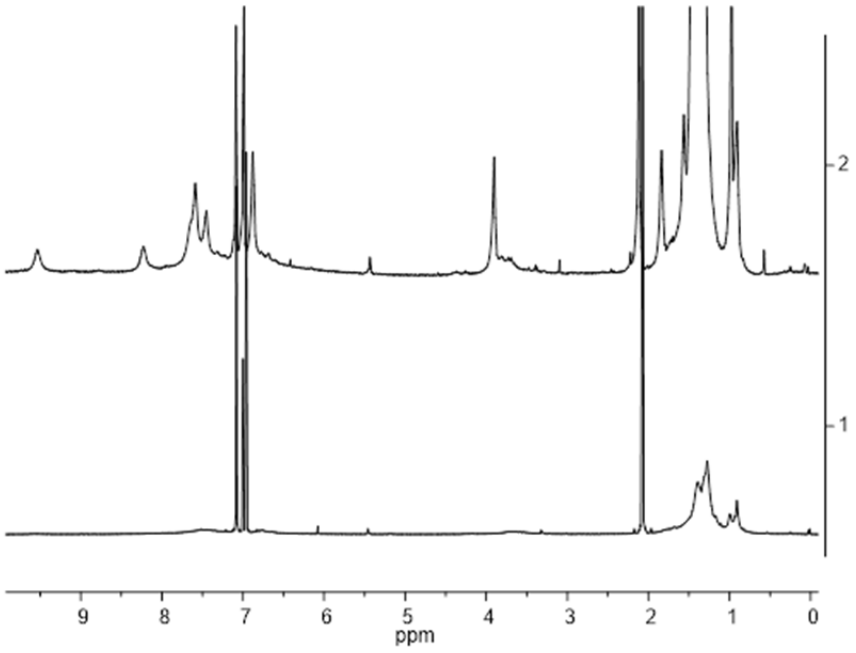

Figure S9: Variable temperature ^{1}H NMR for porphyrin **1a** (toluene) at top) 373 K bottom) 273 K.

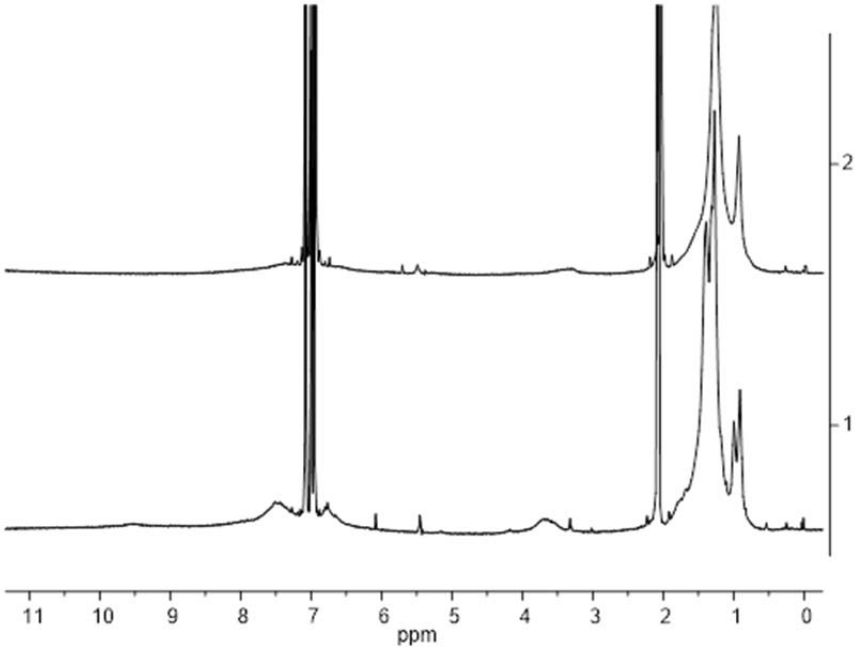

Figure S10: Variable temperature ^{1}H NMR for porphyrin **1a** (toluene) at top) 223 K bottom) 273 K.

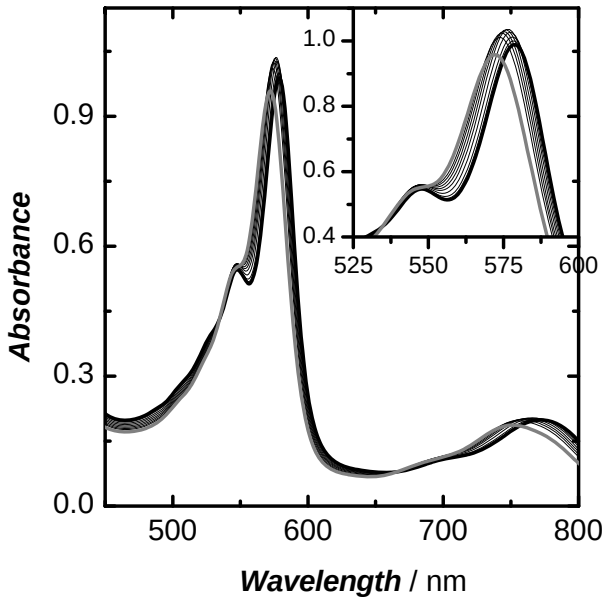

Figure S11: Variable temperature **1a** in toluene (20 μM). Thick black line is 5 °C initial spectrum and thick grey line is final spectrum at 95 °C. Each thin line is at 15 °C, 24 °C, 34 °C, 43 °C, 53 °C, 65 °C and 71 °C

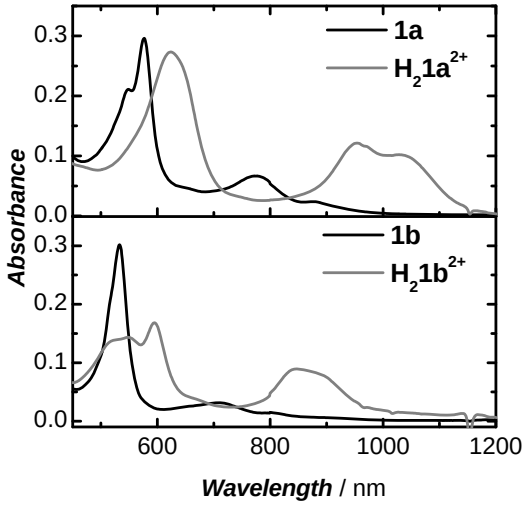

Figure S12: UV-Vis absorption spectra for neutral and diprotonated, acenaphthene fused dithiaporphyrins, **1a** (20 μM) and **1b** (10 μM) in methylene chloride. Protonation was done by addition of excess trifluoroacetic acid.

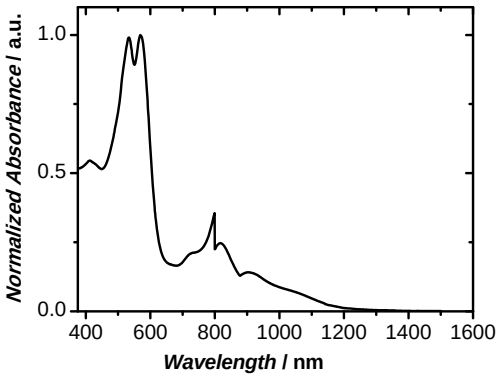

Figure S13: UV-vis spectrum of **1b** in toluene (100 μM) showing a splitting of the Soret-like band.

Table S1: Concentrations and solvent composition of C60 (toluene) added to **1b** (DCM) in Figure 3a in main manuscript.

[1b] M	[C60] M	% DCM
3.0000E-06	0	100.0%
2.9947E-06	1.06E-07	99.8%
2.9893E-06	2.11E-07	99.5%
2.9787E-06	4.21E-07	98.8%
2.9682E-06	6.29E-07	97.7%
2.9577E-06	8.36E-07	96.4%
2.9474E-06	1.04E-06	94.8%
2.8966E-06	2.05E-06	91.7%
2.8000E-06	3.96E-06	86.0%
2.7097E-06	5.74E-06	78.8%
2.6250E-06	7.42E-06	70.8%
2.4706E-06	1.05E-05	61.5%
2.3333E-06	1.32E-05	52.3%
2.1667E-06	1.93E-05	50.4%
2.0222E-06	2.47E-05	47.0%
1.8958E-06	2.93E-05	42.7%
1.7843E-06	3.34E-05	38.1%
1.6852E-06	3.71E-05	33.5%
1.2171E-06	6.10E-05	29.9%
8.7900E-07	8.49E-05	27.0%
6.3483E-07	1.09E-04	24.7%
4.5849E-07	1.33E-04	22.7%
3.3113E-07	1.57E-04	21.0%
2.3915E-07	1.80E-04	19.5%

DFT optimized geometry coordinates for porphyrins **1a-c** boat and chair conformation.

Compound **1a** boat conformation
Energy = -4129.18685267 a.u.
Zero imaginary frequencies

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	-1.27807	2.772514	0.437346
6	-0.71268	3.990839	0.88459
6	0.712675	3.990839	0.88459
6	1.278068	2.772514	0.437346
16	0	1.597402	0.142891
6	-2.63766	2.428066	0.158835
6	3.103971	1.086239	0.035649
6	4.472091	0.68051	-0.28027
6	4.472091	-0.68051	-0.28027
6	3.103971	-1.08624	0.035649
7	2.317211	0	0.217607
6	2.637656	-2.42807	0.158835
6	1.278068	-2.77251	0.437346
6	0.712675	-3.99084	0.88459
6	-0.71268	-3.99084	0.88459
6	-1.27807	-2.77251	0.437346
16	0	-1.5974	0.142891
6	-2.63766	-2.42807	0.158835
6	-3.10397	-1.08624	0.035649
6	-4.47209	-0.68051	-0.28027
6	-4.47209	0.68051	-0.28027
6	-3.10397	1.086239	0.035649
7	-2.31721	0	0.217607
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1	5.30298	-1.34641	-0.46998
1	-5.30298	-1.34641	-0.46998
1	-5.30298	1.34641	-0.46998
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6	3.578136	-3.45603	-0.10384
6	-3.57814	3.456026	-0.10384
6	-3.57814	-3.45603	-0.10384
6	3.578136	3.456026	-0.10384
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6	-4.40844	-4.29164	-0.42475
6	-4.40844	4.291638	-0.42475
6	4.408443	4.291638	-0.42475
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6	6.717752	5.018548	-0.88558
6	4.911783	6.623233	-1.05159
6	7.636614	6.00591	-1.24111
1	7.069562	4.011195	-0.68276
6	5.820104	7.609104	-1.40359
1	3.854525	6.860493	-0.98244
6	7.189891	7.309589	-1.50203
6	-5.34208	5.301213	-0.78261
6	-6.71775	5.018548	-0.88558
6	-4.91178	6.623233	-1.05159
6	-7.63661	6.00591	-1.24111
1	-7.06956	4.011195	-0.68276
6	-5.8201	7.609104	-1.40359
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6	-7.18989	7.309589	-1.50203
6	-5.34208	-5.30121	-0.78261
6	-4.91178	-6.62323	-1.05159
6	-6.71775	-5.01855	-0.88558
6	-5.8201	-7.6091	-1.40359
1	-3.85453	-6.86049	-0.98244
6	-7.63661	-6.00591	-1.24111
1	-7.06956	-4.0112	-0.68276
6	-7.18989	-7.30959	-1.50203
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6	6.717752	-5.01855	-0.88558
6	4.911783	-6.62323	-1.05159
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6	7.189891	-7.30959	-1.50203
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1	5.49275	-8.62331	-1.61211
1	-5.49275	-8.62331	-1.61211
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1	-8.68776	5.749535	-1.31001
1	-5.49275	8.623309	-1.61211
1	5.49275	8.623309	-1.61211
1	8.687764	5.749535	-1.31001
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8	7.999189	8.347978	-1.85614
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6	0	5.970131	1.830363
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1	1.330691	8.720888	3.329935
6	2.425571	7.060651	2.514589
1	3.391279	7.479193	2.786729
6	2.399333	5.797806	1.861529
1	3.333362	5.286178	1.669816
6	-1.18047	5.248504	1.495186
6	-2.39933	5.797806	1.861529
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6	0	-5.97013	1.830363
6	-2.42557	-7.06065	2.514589
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6	1.271469	-7.76126	2.821107
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1	-9.83024	9.072846	-2.27597
6	9.397212	8.115042	-1.9833
1	9.835259	7.791766	-1.03015
1	9.606882	7.366653	-2.75838
1	9.830241	9.072846	-2.27597
6	-9.39721	-8.11504	-1.9833
1	-9.83526	-7.79177	-1.03015
1	-9.60688	-7.36665	-2.75838
1	-9.83024	-9.07285	-2.27597
6	9.397212	-8.11504	-1.9833
1	9.606882	-7.36665	-2.75838
1	9.835259	-7.79177	-1.03015
1	9.830241	-9.07285	-2.27597

Compound **1b** boat conformation

Energy = -3824.53039491 a.u.

Zero imaginary frequencies

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	-1.28564	2.749797	-0.05505
6	-0.71063	3.939694	0.475354
6	0.710634	3.939694	0.475354
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16	0	1.592971	-0.40171
6	-2.63557	2.427889	-0.35553
6	3.083741	1.091458	-0.55192
6	4.367244	0.680782	-1.12524
6	4.367244	-0.68078	-1.12524
6	3.083741	-1.09146	-0.55192
7	2.344271	0	-0.23717
6	2.635573	-2.42789	-0.35553
6	1.285636	-2.7498	-0.05505
6	0.710634	-3.93969	0.475354
6	-0.71063	-3.93969	0.475354
6	-1.28564	-2.7498	-0.05505
16	0	-1.59297	-0.40171
6	-2.63557	-2.42789	-0.35553
6	-3.08374	-1.09146	-0.55192
6	-4.36724	-0.68078	-1.12524
6	-4.36724	0.680782	-1.12524
6	-3.08374	1.091458	-0.55192
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1	5.134638	-1.33529	-1.51561
1	-5.13464	-1.33529	-1.51561
1	-5.13464	1.335292	-1.51561
6	2.635573	2.427889	-0.35553
6	3.619096	3.520465	-0.57137

6	4.871941	3.520509	0.061095	6	0	5.843296	1.569919
6	3.338036	4.576997	-1.46233	6	1.27141	7.564728	2.677205
6	5.812336	4.530264	-0.16846	1	1.330682	8.486481	3.251836
1	5.112264	2.729236	0.765595	6	2.425115	6.893995	2.310242
6	4.263483	5.581688	-1.70805	1	3.391711	7.298508	2.600136
1	2.381118	4.59697	-1.97597	6	2.398706	5.681977	1.567113
6	5.509805	5.567668	-1.06048	1	3.336731	5.199085	1.326038
6	-3.6191	3.520465	-0.57137	6	-1.17969	5.150868	1.177099
6	-4.87194	3.520509	0.061095	6	-2.39871	5.681977	1.567113
6	-3.33804	4.576997	-1.46233	1	-3.33673	5.199085	1.326038
6	-5.81234	4.530264	-0.16846	6	-2.42512	6.893995	2.310242
1	-5.11226	2.729236	0.765595	1	-3.39171	7.298508	2.600136
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1	-2.38112	4.59697	-1.97597	6	-1.27141	7.564728	2.677205
6	-5.50981	5.567668	-1.06048	1	-1.33068	8.486481	3.251836
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6	-4.87194	-3.52051	0.061095	1	-3.33673	-5.19909	1.326038
6	-4.26348	-5.58169	-1.70805	6	0	-5.8433	1.569919
1	-2.38112	-4.59697	-1.97597	6	-2.42512	-6.894	2.310242
6	-5.81234	-4.53026	-0.16846	1	-3.39171	-7.29851	2.600136
1	-5.11226	-2.72924	0.765595	6	-1.27141	-7.56473	2.677205
6	-5.50981	-5.56767	-1.06048	1	-1.33068	-8.48648	3.251836
6	3.619096	-3.52047	-0.57137	6	0	-7.03356	2.318767
6	4.871941	-3.52051	0.061095	6	1.179685	-5.15087	1.177099
6	3.338036	-4.577	-1.46233	6	2.398706	-5.68198	1.567113
6	5.812336	-4.53026	-0.16846	1	3.336731	-5.19909	1.326038
1	5.112264	-2.72924	0.765595	6	2.425115	-6.894	2.310242
6	4.263483	-5.58169	-1.70805	1	3.391711	-7.29851	2.600136
1	2.381118	-4.59697	-1.97597	6	1.27141	-7.56473	2.677205
6	5.509805	-5.56767	-1.06048	1	1.330682	-8.48648	3.251836
1	6.763084	-4.49591	0.352135	6	-7.63506	6.635559	-0.75608
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1	-4.04485	-6.38886	-2.40091	1	-8.22499	5.747724	-1.01871
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1	-4.04485	6.388859	-2.40091	1	-8.22499	-5.74772	-1.01871
1	4.044848	6.388859	-2.40091	1	-8.12451	-7.52731	-1.15121
1	6.763084	4.495909	0.352135	1	-7.55788	-6.71534	0.336277
8	-6.35014	6.599972	-1.3642	6	7.635063	-6.63556	-0.75608
8	-6.35014	-6.59997	-1.3642	1	8.124511	-7.52731	-1.15121
8	6.350139	-6.59997	-1.3642	1	8.224988	-5.74772	-1.01871
8	6.350139	6.599972	-1.3642	1	7.557879	-6.71534	0.336277
6	1.179685	5.150868	1.177099	6	7.635063	6.635559	-0.75608

1	8.224988	5.747724	-1.01871
1	8.124511	7.527312	-1.15121
1	7.557879	6.715342	0.336277

Compound **1c** boat conformation
Energy = -3671.07648835 a.u.
Zero imaginary frequencies

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	-1.27762	2.77322	0.200347
6	-0.71258	3.993704	0.6437
6	0.712575	3.993704	0.6437
6	1.277617	2.77322	0.200347
16	0	1.596443	-0.08874
6	-2.63637	2.427364	-0.07719
6	3.103054	1.085935	-0.19876
6	4.473041	0.680228	-0.51003
6	4.473041	-0.68023	-0.51003
6	3.103054	-1.08594	-0.19876
7	2.315506	0	-0.01946
6	2.636365	-2.42736	-0.07719
6	1.277617	-2.77322	0.200347
6	0.712575	-3.9937	0.6437
6	-0.71258	-3.9937	0.6437
6	-1.27762	-2.77322	0.200347
16	0	-1.59644	-0.08874
6	-2.63637	-2.42736	-0.07719
6	-3.10305	-1.08594	-0.19876
6	-4.47304	-0.68023	-0.51003
6	-4.47304	0.680228	-0.51003
6	-3.10305	1.085935	-0.19876
7	-2.31551	0	-0.01946
1	5.304836	1.345876	-0.69599
1	5.304836	-1.34588	-0.69599
1	-5.30484	-1.34588	-0.69599
1	-5.30484	1.345876	-0.69599
6	2.636365	2.427364	-0.07719
6	3.578455	-3.45406	-0.34371
6	-3.57846	3.454055	-0.34371
6	-3.57846	-3.45406	-0.34371
6	3.578455	3.454055	-0.34371
6	4.410055	-4.28652	-0.66693
6	-4.41006	-4.28652	-0.66693
6	-4.41006	4.286518	-0.66693
6	4.410055	4.286518	-0.66693
6	5.351166	5.291482	-1.02722
6	6.726825	4.988988	-1.12626
6	4.922013	6.610071	-1.29563
6	7.641809	5.977378	-1.48261
1	7.063984	3.977268	-0.92046
6	5.845722	7.591825	-1.64919
1	3.86467	6.847222	-1.22637
6	7.206575	7.281248	-1.74464
6	-5.35117	5.291482	-1.02722
6	-6.72683	4.988988	-1.12626
6	-4.92201	6.610071	-1.29563
6	-7.64181	5.977378	-1.48261
1	-7.06398	3.977268	-0.92046
6	-5.84572	7.591825	-1.64919
1	-3.86467	6.847222	-1.22637
6	-7.20658	7.281248	-1.74464
6	-5.35117	-5.29148	-1.02722
6	-4.92201	-6.61007	-1.29563
6	-6.72683	-4.98899	-1.12626
6	-5.84572	-7.59183	-1.64919
1	-3.86467	-6.84722	-1.22637
6	-7.64181	-5.97738	-1.48261
1	-7.06398	-3.97727	-0.92046
6	-7.20658	-7.28125	-1.74464
6	5.351166	-5.29148	-1.02722
6	6.726825	-4.98899	-1.12626
6	4.922013	-6.61007	-1.29563
6	7.641809	-5.97738	-1.48261
1	7.063984	-3.97727	-0.92046
6	5.845722	-7.59183	-1.64919
1	3.86467	-6.84722	-1.22637
6	7.206575	-7.28125	-1.74464
1	8.697615	-5.73101	-1.55588
1	5.501612	-8.60249	-1.85442
1	-5.50161	-8.60249	-1.85442
1	-8.69762	-5.73101	-1.55588
1	-8.69762	5.73101	-1.55588
1	-5.50161	8.602487	-1.85442
1	5.501612	8.602487	-1.85442
1	8.697615	5.73101	-1.55588
6	1.180472	5.252977	1.249998

6	0	5.975526	1.582532
6	1.271374	7.768904	2.569084
1	1.330569	8.729637	3.075722
6	2.425699	7.067347	2.265155
1	3.391256	7.486097	2.537187
6	2.399396	5.802818	1.615828
1	3.333575	5.290365	1.427225
6	-1.18047	5.252977	1.249998
6	-2.3994	5.802818	1.615828
1	-3.33358	5.290365	1.427225
6	-2.4257	7.067347	2.265155
1	-3.39126	7.486097	2.537187
6	0	7.216175	2.244822
6	-1.27137	7.768904	2.569084
1	-1.33057	8.729637	3.075722
6	-1.18047	-5.25298	1.249998
6	-2.3994	-5.80282	1.615828
1	-3.33358	-5.29037	1.427225
6	0	-5.97553	1.582532
6	-2.4257	-7.06735	2.265155
1	-3.39126	-7.4861	2.537187
6	-1.27137	-7.7689	2.569084
1	-1.33057	-8.72964	3.075722
6	0	-7.21618	2.244822
6	1.180472	-5.25298	1.249998
6	2.399396	-5.80282	1.615828
1	3.333575	-5.29037	1.427225
6	2.425699	-7.06735	2.265155
1	3.391256	-7.4861	2.537187
6	1.271374	-7.7689	2.569084
1	1.330569	-8.72964	3.075722
1	-7.92315	8.049544	-2.02281
1	7.923153	8.049544	-2.02281
1	7.923153	-8.04954	-2.02281
1	-7.92315	-8.04954	-2.02281

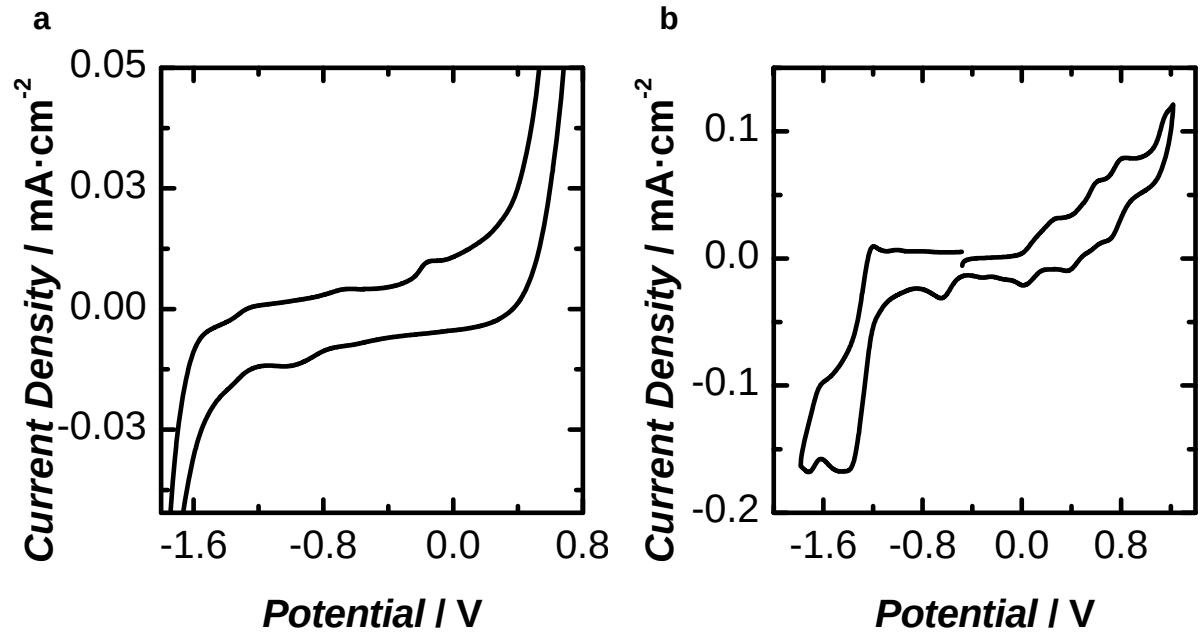

Figure S14. Cyclic voltammograms of dithiaporphyrins a) **1a** and b) **1b** in methylene chloride (3 mM) containing 0.1 M $(n\text{Bu})_4\text{NPF}_6$ at a glassy carbon electrode at a scan rate of 100 mVs^{-1} versus Fc/Fc^+.

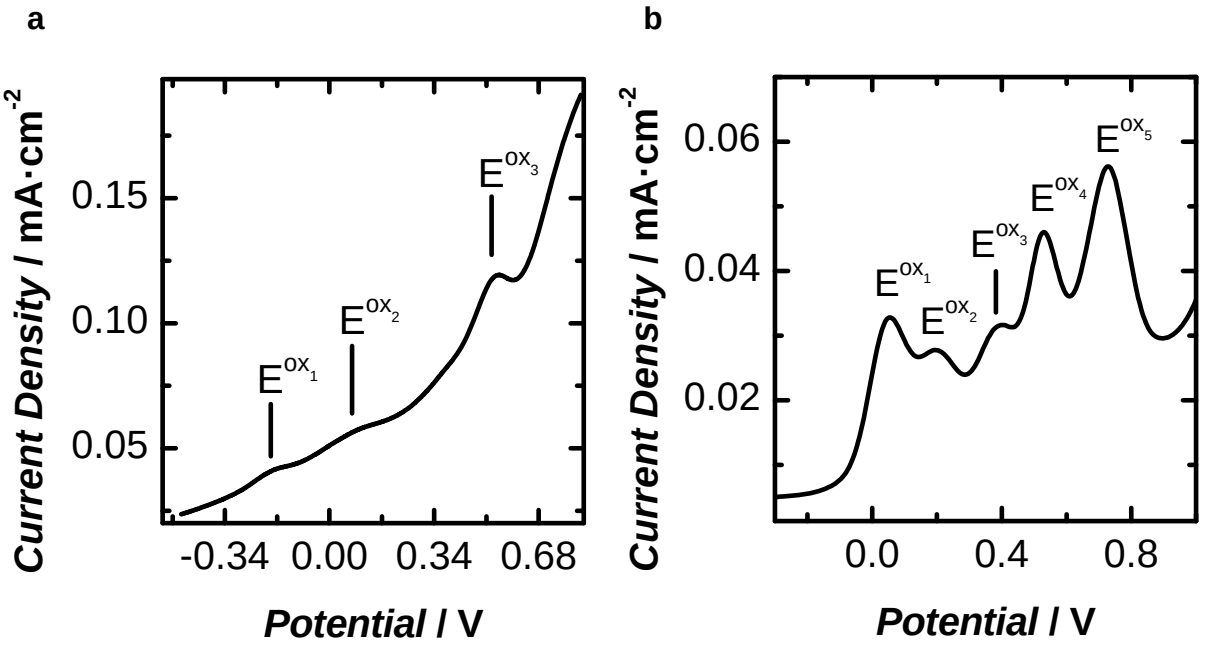

Figure S15. Differential pulse voltammograms of dithiaporphyrins a) **1a** and b) **1b** in methylene chloride (3 mM) containing 0.1 M $(n\text{Bu})_4\text{NPF}_6$ at a glassy carbon electrode at a scan rate of 100 mVs^{-1} versus Fc/Fc^+.